

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 737 773 A1**

(12)

**EUROPEAN PATENT APPLICATION**

published in accordance with Art. 158(3) EPC

(43) Date of publication:

16.10.1996 Bulletin 1996/42

(51) Int. Cl.<sup>6</sup>: **D06M 13/292**, D06M 13/188,  
D06M 15/277

(21) Application number: 95903962.9

(86) International application number:  
PCT/JP94/02223

(22) Date of filing: 27.12.1994

(87) International publication number:  
WO 95/18258 (06.07.1995 Gazette 1995/29)

(84) Designated Contracting States:

AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL  
PT SE

(30) Priority: 28.12.1993 JP 353613/93

(71) Applicant: **DAIKIN INDUSTRIES, LTD.**  
Kita-ku, Osaka 530 (JP)

(72) Inventors:

• **ITAMI, Yasuo**  
1-1, Nishihitotsuya Settsu-shi Osaka 566 (JP)

• **MASUTANI, Tetsuya**

1-1, Nishihitotsuya Settsu-shi Osaka 566 (JP)

(74) Representative: **Hansen, Bernd, Dr. Dipl.-Chem.**  
et al  
**Hoffmann, Eitle & Partner,**  
Patentanwälte,  
Arabellastrasse 4  
81925 München (DE)

**(54) METHOD OF TREATING TEXTILE PRODUCTS AND TEXTILE PRODUCTS THUS TREATED**

(57) A fiber is firstly treated with a metal salt and a phosphoric acid compound, or treated with a carboxylic acid-metal complex obtained from a metal salt and a carboxylic acid in a first stage, and then treated with a usual fluorine-containing water- and oil-repellent in a second stage. According to the present invention, the water-repellency which is durable to washing and friction is imparted to a textile, and the touch, the feeling and the flexibility of the textile itself are not deteriorated.

**EP 0 737 773 A1**

## Description

## FIELD OF THE INVENTION

The present invention relates to a method for treatment of a textile, and a treated textile. More particularly, it relates to a method for treatment of a textile, which method maintains durable water- and oil-repellency even after long-term use including the washing and the like and further maintains a touch, a feeling and a flexibility of fiber itself, by a modification treatment of the textile.

## RELATED ART

It has hitherto been known that a fluorine-containing compound having a fluoroalkyl group gives excellent water- and oil-repellency to a textile. Particularly, an acrylic polymer treating agent having a fluoroalkyl group has been practically used. However, in a treatment using the acrylic polymer treating agent having a fluoroalkyl group, there is a disadvantage that a touch, a feeling and a flexibility of the treated textile are remarkably deteriorated and the resultant water repellency is remarkably deteriorated by the washing or abrasion. As an attempt of enhancing a durability of a water- and oil repellency, a combined agent has been used on the treatment, together with the acrylic polymer having the fluoroalkyl group. Examples of combined agent include a melamine resin, a urea resin and the like. When these resins are used in combination, the durability is improved in comparison with the case when using the polymer alone, but the touch, feeling and flexibility of fiber itself are liable to be deteriorated. Accordingly, it can be said that the durability and the touch, feeling and flexibility of fiber itself are contrary each other when using the fluorine-containing polymer. Japanese Patent Kokai Publication No. 98568/1993 discloses that animal hair fibers are treated with an alkylphosphate salt to impart the water repellency and flexibility to the animal hair fibers. However, the treated fibers are inferior in durability because they are not treated with a fluorine-containing water- and oil-repellent.

Hitherto, a chromium complex of carboxylic acid has also been used as a processing agent for a textile or paper for the purpose of imparting a water repellency. Particularly, a chromium complex of carboxylic acid having a perfluoroalkyl group has been used for the purpose of imparting an oil repellency in addition to the water repellency (cf. Japanese Patent Kokoku Publication Nos. 466/1958 and 3274/1969). However, an effect of these chromium complexes is not always sufficient, and a further enhancement in effect has been required.

## PROBLEMS TO BE SOLVED BY THE INVENTION

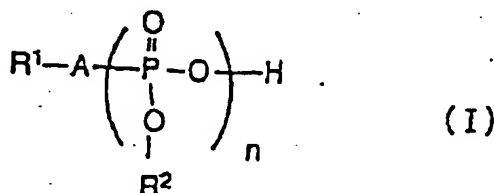
An object of the present invention is to maintain a durable water- and oil-repellency even after long-term use including the washing and the like, and to maintain a touch, a feeling and a flexibility of fiber itself even after the treatment of textile.

## MEANS FOR SOLVING THE PROBLEMS

The present invention provides a method for treatment of a textile, which comprises:

(A)

(i) treating a textile with a modifier of a phosphoric acid derivative represented by the general formula:



wherein  $\text{R}^1$  and  $\text{R}^2$  are, the same or different, a hydrogen atom or a saturated or unsaturated straight-chain or branched hydrocarbon group having 4 to 20 carbon atoms (an oxygen atom, a nitrogen atom, a sulfonyl group or an aromatic ring may be present between carbon atoms), provided that  $\text{R}^1$  and  $\text{R}^2$  are not simultaneously a hydrogen atom;

A is an oxygen atom, a sulfur atom or a direct bond; and

n is 1 or 2,

or a salt thereof before or after treating the textile with a fixing agent of a metal salt compound, or

(ii) treating a textile with a metal complex formed from a metal salt compound and a carboxylic acid represented by the general formula:



wherein  $R^3$  is a saturated or unsaturated straight-chain or branched hydrocarbon or fluoroalkyl group having 4 to 28 carbon atoms (an oxygen atom, a nitrogen atom, a sulfonyl group or an aromatic ring may be present between carbon atoms); and then

(B) treating the textile with a fluorine-containing water- and oil-repellent.

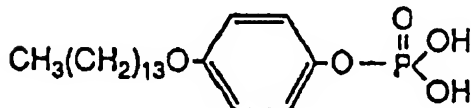
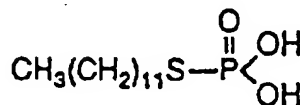
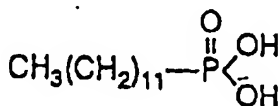
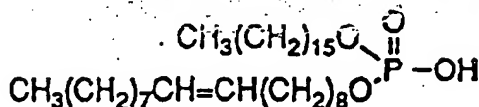
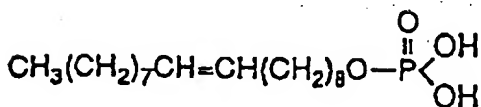
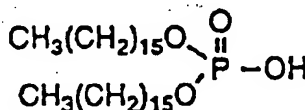
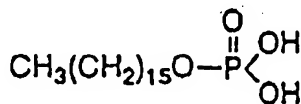
The present also provide a textile treated by the above method for treatment.

In the present invention, the term "treatment" used herein means that a textile is contact with a treating liquid containing the modifier, the fixing agent, the metal complex or the fluorine-containing water- and oil-repellent. The treatment may be conducted, for example, by an immersion, an impregnation, a pad method, a coating method and the like.

In the first stage of treatment, the textile may be treated with the modifier after treated with the fixing agent. Alternatively, a textile may be treated with the fixing agent after treated with the modifier.

The modifier used in the first stage of treatment is the phosphoric acid derivative represented by the above general formula (I) or the salt thereof. The phosphoric acid derivative is a compound having a P-OH bond and a hydrocarbon group. The hydrocarbon group usually means a saturated or unsaturated straight-chain or branched aliphatic hydrocarbon group, and includes those in which an oxygen atom, a nitrogen atom, a sulfonyl group or an aromatic ring exists in a carbon-carbon bond. It is preferred that the hydrocarbon group is an alkyl group. Examples of the salt of the phosphoric acid derivative include a monovalent metal salt such as a sodium salt, a potassium salt, a lithium salt, etc.; an organic amine salt such as a diethanolamine salt, a triethylamine salt, a propylamine salt, a morpholine salt, etc.; and an ammonium salt. A molecular weight of the phosphoric acid derivative or the salt thereof varies depending on the general formula, but is preferably not more than 2000.

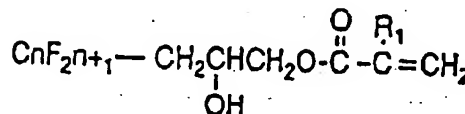
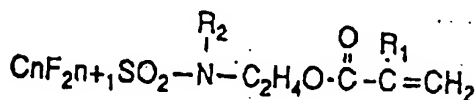
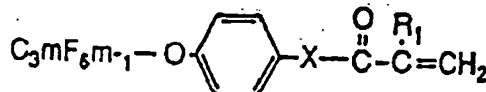
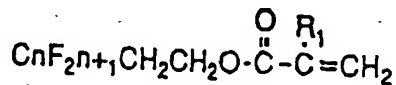
Specific examples of the phosphoric acid derivative are as follows, but are not limited thereto.



The metal in the metal salt compound as the fixing agent used in the first stage of treatment may be a polyvalent (divalent or more) metal which bonds ionically to a hydroxyl group bonding to a phosphoric atom. Usually, chromium, zirconium, titanium, aluminum and the like are preferred. It is preferred that the metal salt compound is water-soluble

one. For example, chloride, nitrate, sulfate, hydroxide and the like are preferred. Among them, basic chromium sulfate and basic zirconium sulfate are particularly preferred in view of durability.

In the present invention, the fluorine-containing water- and oil-repellent used in the second step of treatment is a fluorine-containing compound having a perfluoroalkyl group. The fluorine-containing compound may be a known fluorine-containing polymer having a side chain of a perfluoroalkyl group. For example, the following monomers forming polymers or copolymer can be used.

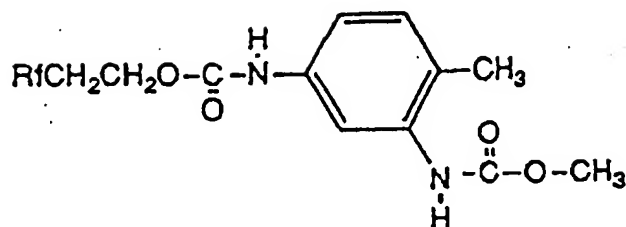


wherein  $\text{R}_1$  is a hydrogen atom or a methyl group;  $\text{R}_2$  is a lower alkyl group; X is a divalent organic group; m is an integer of 1 to 4; and n is an integer of 5 to 21.

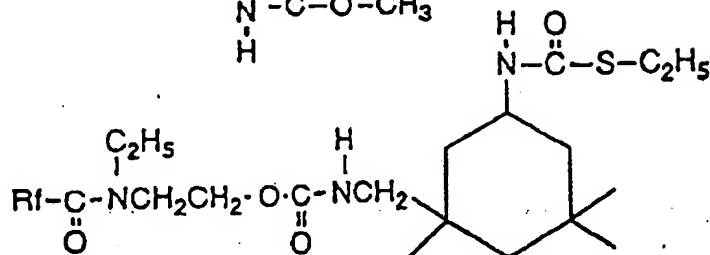
An average molecular weight of the fluorine-containing polymer is usually from 5,000 to 500,000.

The fluorine-containing compound may be a fluorine-containing urethane compound or a fluorine-containing ester compound, and examples thereof include the followings.

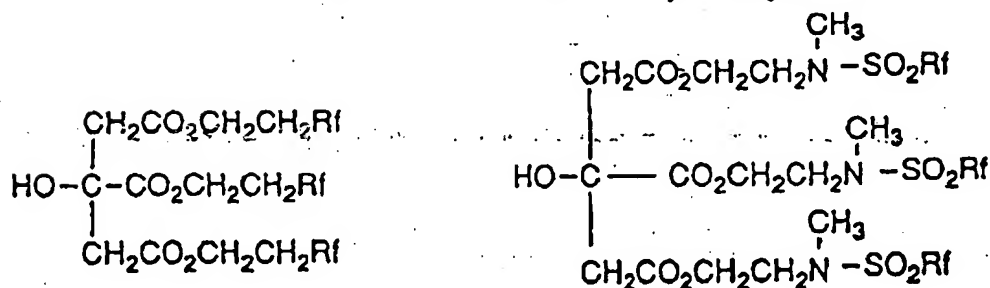
5



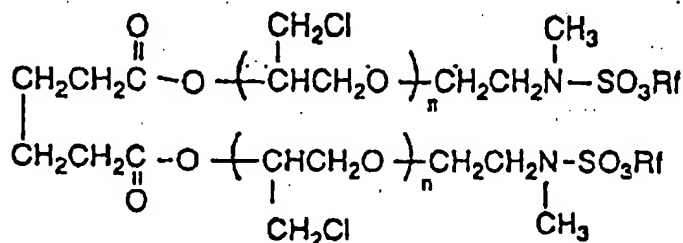
10



15



25



30

35

wherein Rf is  $\text{C}_m\text{F}_{m+1}$  (m is an integer of 5 to 21); and n is 0 to 4.

The fluorine-containing water- and oil-repellent may be used in combination with various combined agents, and examples of the combined agent include a melamine resin, a urea resin, a blocked isocyanate, glyoxal and the like.

40

In the first stage of treatment of the present invention, the textile is treated with the modifier and the fixing agent. The use order of the modifier and fixing agent may be freely selected as described hereinafter. Examples of the method for treatment using the modifier and the fixing agent include the following methods (1), (2) and (3).

45

(1) A method comprising firstly treating with the fixing agent and then treating with the modifier will be explained. The textile is immersed in the fixing agent solution and removed from a bath and then water is swished off from the textile. After the textile is immersed in a modifier solution, an acid solution is added to the same bath to adjust the pH to 1 to 5, preferably from 3 to 4, followed by standing. The textile is swished to remove water, washed sufficiently with water, swished to remove water and then dried. Alternatively, the textile is immersed in the modifier solution and, after swish off of water, the textile is immersed in an acid solution (pH: 1 to 5), swished for removing water, washed sufficiently with water, swished for removing water and then dried.

50

55

(2) The order of the immersion in the fixing agent solution and the immersion in the modifier solution may be reversed. Firstly, the textile is immersed in the modifier solution, removed from the bath and then swished to remove water. After the textile is immersed in the fixing agent solution, an acid solution is added to the same bath to adjust the pH to 1 to 5, preferably from 3 to 4, followed by standing. The textile is swished to remove water, washed sufficiently with water, swished to remove water and then dried. Alternatively, the textile is immersed in the fixing agent solution and, after swish off of water, the textile is immersed in the acid solution, swished to remove water, washed sufficiently with water, swished to remove water and then dried.

(3) It is also possible to conduct a series of these treatments in the same bath. For example, after the textile is immersed in the fixing solution, the modifier is added in the bath and the textile is immersed in the bath. An acid

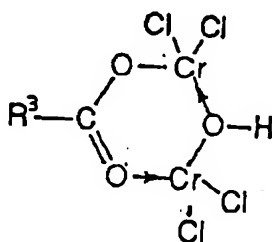
solution is added to adjust the pH to 1 to 5, preferably from 3 to 4, followed by standing. The textile is swished to remove water, washed sufficiently with water, swished to remove water and then dried. The fixing agent solution may be added after the textile is immersed in the modifier solution.

In the above methods (1), (2) and (3), the solution of the metal salt compound as the fixing agent is an aqueous solution of 0.01 to 10% by weight, preferably from 0.03 to 3% by weight. A temperature of the fixing agent solution is usually from 20 to 70°C. A solution of the phosphoric acid derivative as the modifier is an aqueous solution or a lower alcohol solution of 0.01 to 10% by weight, preferably from 0.03 to 3% by weight. Examples of the lower alcohol include methanol, ethanol, isopropyl alcohol and the like. A temperature of the modifier solution is usually from 5 to 90°C, preferably from 20 to 70°C.

The acid solution used for the immersion or the adjustment of pH is a solution, preferably aqueous solution, containing a mineral acid such as hydrochloric acid and sulfuric acid or an organic acid such as formic acid, acetic acid and propionic acid. A concentration of the acid solution is not specifically limited, but is usually from 0.05 to 30% by weight, preferably from 0.1 to 5% by weight. A temperature of the acid solution is usually from 5 to 90°C, preferably from 20 to 70°C. An immersion time in each of the fixing agent solution, the modifier solution and the acid solution is usually at least 10 seconds, preferably from 1 to 120 minutes, more preferably from 1 to 30 minutes. A retention time in the bath adjusted to the pH of 1 to 5 is usually at least 10 seconds, preferably from 1 to 30 minutes. A drying temperature is usually from 10 to 70°C, preferably room temperature. The drying time varies depending on the drying condition (particularly, the drying temperature), but is usually within 24 hours, preferably from 0.1 to 10 hours. In case of the same bath shown in the above method (3), a weight ratio of the fixing agent to the modifier in the bath is usually from 0.1:1 to 10:1.

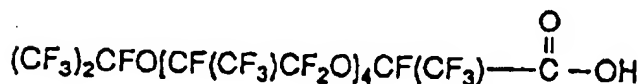
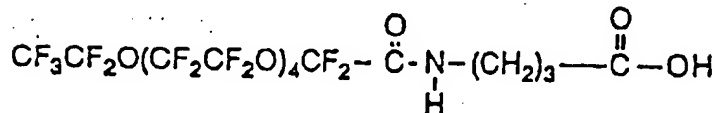
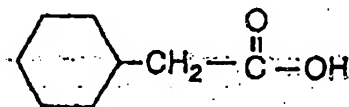
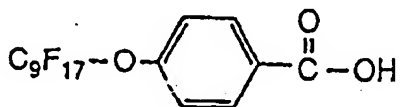
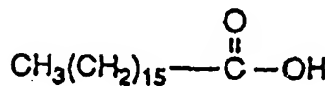
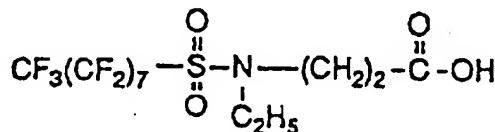
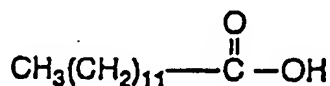
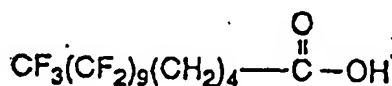
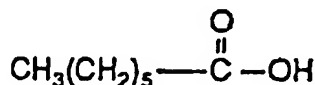
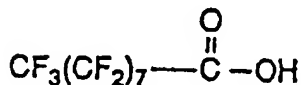
Then, a method for treatment of fibers using the carboxylic acid derivative will be explained. A carboxylic acid-metal complex is obtained by reacting the metal salt compound with the carboxylic acid.

For example, a chromium complex is obtained by reacting a carboxylic acid with a chromium compound. The chromium compound is a compound represented by the formula:  $\text{Cr}(\text{OH})\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ . The chromium complex is, for example,



wherein  $\text{R}^3$  is as defined above. The chromium complex is obtained by heating the carboxylic acid together with the chromium compound in the presence or absence of a solvent.

Specific examples of the carboxylic acid include the followings, but are not to be limited thereto.



The metal salt compound in the metal complex may be the metal salt compound described above as in the fixing agent.

In the method of the present invention, the textile is firstly treated with a treating agent comprising the metal complex of carboxylic acid, in the first stage of treatment. In the method of the present invention, the textile is immersed in an aqueous solution (liquid temperature: 20 to 75°C, preferably from 30 to 50°C) containing the metal complex of carboxylic acid in an amount of 0.01 to 30% by weight, preferably from 0.1 to 10% by weight, for at least 10 seconds, preferably from 1 to 120 minutes, removed from the bath, swished for removing water and then dried. A drying temperature can be adjusted within the range from 10 to 140°C, but it is practically sufficient to air-dry at room temperature.

In the first stage of treatment, the aqueous solution may contain an acid. Examples of the acid include mineral acids such as hydrochloric acid and sulfuric acid and organic acids such as formic acid, acetic acid and propionic acid.

The textile which has already been subjected to the first stage of treatment is treated with a usual fluorine-containing water- and oil-repellent as described hereinafter, in the second stage (B) of treatment. The method may be a method which has hitherto been used. For example, the treatment is conducted by an immersion, a pad method, a coating method or the like, followed by drying. In that case, the combined agent such as the melamine resin and the urea resin may be used in combination. If necessary, a heat treatment, a calendaring and the like may be conducted. It is also possible to use a treating agent (e.g. a silicon compound) other than the fluorine-containing compound in combination.

The form of the fluorine-containing water- and oil-repellent may be an emulsion or a solution in an organic solvent. In case of the emulsion, it is preferred to add, to the emulsion, a water-soluble lower alcohol or ketone (isopropyl alcohol is particularly preferred) in an amount of 0.1 to 10% by weight, preferably from 1 to 5% by weight based on the emulsion, in view of penetration of the fluorine-containing water- and oil-repellent.

The second stage of treatment can be applied to any textile. For example, a resultant carpet (or fabric) may be subjected to the second stage of treatment. Alternatively, the second stage of treatment can be conducted on raw yarns or raw hairs used for the carpet, and the carpet can be produced by using the treated raw yarns or raw hairs. The raw

yarns and raw hairs may be subjected to the first stage of treatment and then the resultant carpet may be subjected to the second stage of treatment.

In the present invention, there is no disadvantage that the water- and oil-repellency is obtained only at the surface of the textile fabric because the phosphoric acid derivative or carboxylic-metal complex is penetrated into the interior of a fiber bundle and then fixed. It is possible to impart the advantageous effect in the interior of textile even if the textile has a large thickness. Since the second stage of treatment is further conducted by using the fluorine-containing water- and oil-repellent, the durability becomes stronger. When using the phosphoric acid derivative, the deterioration of the feeling and flexibility of the textile which has not hitherto been avoided by using the fluorine-containing water- and oil-repellent alone, is improved surprisingly. Even if the fluorine-containing water- and oil-repellent is used in combination with the combined agent such as a melamine resin and a blocked isocyanate, there can be obtained an unexpected effect of maintaining the same feeling as that of the non-treated textile. These effects are not influenced by various forms of the textile, and the same effect can be obtained in a fiber, a yarn, a woven fabric, a knitted fabric, a nonwoven fabric, an artificial leather of superfine fibers and the like.

In the present invention, the textile to be treated includes a yarn, a woven fabric, a knitted fabric, a nonwoven fabric, an artificial leather and the like which are formed from the fiber, in addition to the textile having the form of the fiber as such. As the fiber, there can be used chemical fibers including synthetic fibers such as polyester and nylon in addition to natural fibers such as cotton, wool and silk. It is also possible to use a textile blend of natural fibers and synthetic fibers. The woven fabric and artificial leather comprising superfine fibers, which have recently been remarkably developed, are suitable for the present invention in view of the fact that the feeling and touch are considered to be important. The superfine fibers usually have a fineness of not more than 1 denier, preferably not more than 0.8 denier, more preferably from 0.8 to 0.0001 denier, most preferably from 0.1 to 0.001 denier.

The textile obtained by the present invention has the above excellent advantages and, therefore, it is suitably used for applications where water and oil repellency as well as stainproofing properties are required. The textile which is suitable for the present invention may be, for example, a carpet. The material of the carpet may be a polyamide such as nylon, a polyester, an acryl, a wool and the like, and is not specifically limited. The present invention is particularly effective for a nylon carpet which is usually used under a severe condition. The structure, the weaving type, the pile length of the carpet are not specifically limited.

The textile obtained according to the present invention can be used for outdoor applications exposed to rainwater. Examples thereof include a tent, an automobile cover, a motorbike cover, a hood for rear deck of truck, a coated sheet for construction, an umbrella and clothes (particularly, rainwears such as a raincoat and a poncho).

Applications such as the textile which is not easily cleaned, the textile which is easily stained, and the textile which can not be washed many times are preferred. For example, the present invention can be used for the textiles used for a cover of a cap, a foot wear (e.g. shoes, slippers), a bag, a pouch or a seat (e.g. a car seat, a seat, a sofa and a chair), interior goods such as a curtain, a carpet, a wall and ceiling of buildings and vehicles (e.g. an automobile, a train, an aircraft and a ship) and various displays.

#### PREFERRED EMBODIMENT OF THE INVENTION

The present invention will be illustrated by the following Examples and Comparative Examples.

The water repellency shown in the Examples and Comparative Examples is measured according to JIS-L-1092-1977 and expressed by the numeral shown in Table 1. The oil repellency is measured by a method according to AATCC TM-118-1975, and a maximum number of oil wherein no penetration is observed after 30 minutes from dropping several drops of oils having different surface tensions shown in Table 2 is expressed as the oil repellency.

Table 1

Water repellency	State
100	No wet on the surface
90	Slight wet on the surface
80	Partial wet on the surface
70	Wet on the surface
50	Wet over the whole surface
0	Complete wet on the front and back surfaces



Table 2

Oil repellency	Surface tension	Test solution
0	-	Inferior to 1
1	31.45	Nujol
2	29.6	Nujol/n-hexadecane = 65:35 (volume %)
3	27.3	n-Hexadecane
4	26.35	n-Tetradecane
5	24.7	n-Dodecane
6	23.5	n-Decane
7	21.4	n-Octane
8	19.75	n-Heptane

The washing resistance was measured according to JIS-L-0217-103 and was expressed by the water repellency and oil repellency before and after washing 20 times. The superscript "+" to the water repellency and oil repellency represents that the result is slightly better than said water repellency and said oil repellency.

The water absorption properties are measured according to JIS-K-6550-1976. That is, each sample is immersed in a distilled water for 30 minutes and the water absorption properties are represented by an increase in weight (%) before and after immersion.

The water resistance is measured according to JIS-K-6550-1976. That is, a sample is attached to a water resistance test machine (manufactured by YASUDA SEIKI SEISAKUSHO CO., LTD.) having a structure that a constant pressure is applied to a bore having a diameter of 50 mm, and then a water column is gradually increased. The water resistance is represented by a height of the water column at which water leaks onto the surface of the sample.

The feeling (sensual evaluation) of the treated fibers was evaluated according to the criteria shown in Table 3.

Table 3

Indication	Feeling
○	Soft
△	Slightly hard
X	Hard

Example 1 (in case (i) that the treatment is conducted using a phosphoric acid derivative and a fixing agent)

#### First stage of treatment

A fabric consisting of superfine fibers (Artificial Leather SOFRINATIAL (trade name) manufactured by KURARAY CO., LTD) was immersed at 30°C in an aqueous 0.5% solution (bath ratio: 10:1) of basic chromium sulfate (BAY-CHROME F (trade name) manufactured by BAYER AG) and then subjected to a rotating treatment using a dyeing test machine (manufactured by TSUZII SENKI KOGYO CO., LTD.) for 30 minutes. After swish off of water, the fabric was immersed at 50°C in an aqueous 0.5% solution (bath ratio: 10:1) of a compound 1 (phosphoric acid derivative) shown in Table 4 and then subjected to a rotating treatment for 30 minutes. After the pH was adjusted to 3 by adding a 0.3% aqueous formic acid solution to the bath, the fabric was rotated for 30 minutes, swished to remove water, washed with water at 40°C and then dried at room temperature.

Second stage of treatment

A fluorine-containing water- and oil-repellent (TEXGUARD TG-520 (trade name) manufactured by DAIKIN INDUSTRIES, LTD.) was diluted with tap water so that a solid content was 1%. Further, 2% of a blocked isocyanate (ELASTRON BN-69 manufactured by DAIICHI KOGYO SEIYAKU CO., LTD.) as a combined agent, 0.2% of a catalyst (ELASTORON CATALYST manufactured by DAIICHI KOGYO SEIYAKU Co., LTD.) and 3% of isopropyl alcohol were added to prepare a treating liquid. The test fabric which had already been subjected to the first stage of treatment was immersed in the resultant treating liquid, squeezed with a mangle to adjust a wet pickup to 50%, dried at 110°C for 3 minutes and then heat-treated at 160°C for one minute.

The feeling, water repellency, oil repellency, water absorption property and water resistance before and after washing were measured. The results are shown in Table 5.

Comparative Example 1Only second stage of treatment

The textile sample used in Example 1 was subjected to only the same treatment as the second stage of treatment used in Example 1. The feeling, water repellency, oil repellency, water absorption property and water resistance before and after washing were measured. The results are shown in Table 5.

Comparative Example 2Only first stage of treatment

The textile sample used in Example 1 was subjected to only the same treatment as the first stage of treatment used in Example 1. The feeling, water repellency, oil repellency, water absorption property and water resistance before and after washing were measured. The results are shown in Table 5.

Table 4

Compound 1:

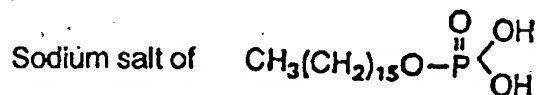


Table 5

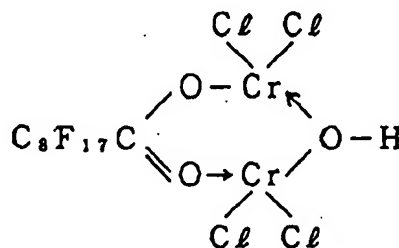
		Feeling	Water repellency	Oil repellency	Water absorption property (%)	Water resistance (cm)
Example 1	L0	O	100+	4	5.8	140
	L20	O	70	1	29.4	114
Com. Ex. 1	L0	X	100+	4	10.6	109
	L20	X	50	0	72.6	79
Com. Ex. 2	L0	O	70+	0	10.4	76
	L20	O	50	0	79.0	71

(Note) L0 and L20 respectively indicate "before washing" and "after washing 20 times".

Example 2 (in case (ii) that the treatment is conducted using a carboxylic acid-metal complex)

#### First stage treatment

A fabric consisting of supertine fibers (Artificial Leather SOFRINATIAL (trade name) manufactured by KURARAY CO., LTD) was immersed in an aqueous solution (bath ratio: 250%) containing 2% (solid content) of a perfluoroalkyl group-containing carboxylic acid-chromium complex (SCOTCHGUARD 233A manufactured by 3M CO.) of the formula:



and 0.4% of formic acid and then subjected to a rotating treatment at 40°C using a dyeing test machine (manufactured by TSUZII SENKI KOGYO CO., LTD.) for 30 minutes. After swish off of water, the fabric was squeezed so that a wet pickup was 80%, and then the fabric was air-dried at room temperature.

#### Second stage of treatment

A fluorine-containing water- and oil-repellent (TEXGUARD TG-520 manufactured by DAIKIN INDUSTRIES, LTD.) was diluted with tap water so that a solid content was 1%. Further, 2% of a blocked isocyanate (ELASTRON BN-69 manufactured by DAIICHI KOGYO SEIYAKU CO., LTD.) as a combined agent, 0.2% of a catalyst (ELASTORON CATALYST manufactured by DAIICHI KOGYO SEIYAKU CO., LTD.) and 3% of isopropyl alcohol were added to prepare a treating liquid. The test fabric which had already been subjected to the first stage of treatment was immersed in the resultant treating liquid, squeezed with a mangle to adjust a wet pickup to 50%, dried at 110°C for 3 minutes and then heat-treated at 160°C for one minute.

The feeling, water repellency, oil repellency, water absorption property and water resistance before and after washing were measured. The results are shown in Table 6.

#### Comparative Example 3

##### Only second stage of treatment

The textile sample used in Example 2 was subjected to only the same treatment as the second stage of treatment used in Example 2, except that the solid content of the fluorine-containing water- and oil-repellent in the liquid was increased to two times that of Example 2. The feeling, water repellency, oil repellency, water absorption property and water resistance before and after washing were measured. The results are shown in Table 6.

#### Comparative Example 4

##### Only first stage of treatment

The textile sample used in Example 2 was subjected to only the same treatment as the first stage of treatment used in Example 2, except that the solid content of the carboxylic acid-chromium complex in the solution was increased to two times that of Example 2. The feeling, water repellency, oil repellency, water absorption property and water resistance before and after washing were measured. The results are shown in Table 6.

Table 6

		Water repellency	Oil repellency	Water absorption property (%)	Water resistance (cm)
Example 2	L0	100+	4	5.3	150
	L20	70	1	6.8	112
Com. Ex. 3	L0	100+	4	10.6	109
	L20	50	0	72.6	79
Com. Ex. 4	L0	80+	3	7.1	124
	L20	50	0	14.2	109

(Note) L0 and L20 respectively indicate "before washing" and "after washing 20 times".

## EFFECT OF THE INVENTION

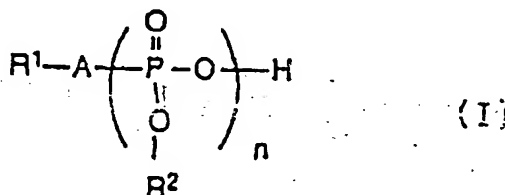
According to the present invention, the durable water repellency can be maintained even after a long-term use including washing and friction and, furthermore, the touch, the feeling and the flexibility of fiber itself can be maintained even after a treatment of a textile when treated with a phosphoric acid derivative and a fixing agent. The present invention solves the problem of durability and the problem of flexibility which were contrary each other, while said problems occurs when using a conventional fluorine-containing water- and oil-repellent.

## Claims

1. A method for treatment of a textile, which comprises:

(A)

(i) treating a textile with a modifier of a phosphoric acid derivative represented by the general formula:



wherein  $R^1$  and  $R^2$  are, the same or different, a hydrogen atom or a saturated or unsaturated straight-chain or branched hydrocarbon group having 4 to 20 carbon atoms (an oxygen atom, a nitrogen atom, a sulfonyl group or an aromatic ring may be present in a carbon-carbon bond), provided that  $R^1$  and  $R^2$  are not simultaneously a hydrogen atom;

A is an oxygen atom, a sulfur atom or a direct bond; and  
n is 1 or 2,

or a salt thereof before or after treating the textile with a fixing agent of a metal salt compound, or  
(ii) treating a textile with a metal complex formed from a metal salt compound and a carboxylic acid represented by the general formula:



wherein  $R^3$  is a saturated or unsaturated straight-chain or branched hydrocarbon or fluoroalkyl group having 4 to 28 carbon atoms (an oxygen atom, a nitrogen atom, a sulfonyl group or an aromatic ring may be present in a carbon-carbon bond); and then

(B) treating the textile with a fluorine-containing water- and oil-repellent.

2. The method for treatment of the textile according to claim 1 wherein the metal salt compound is a salt of chromium, zirconium, titanium or aluminum.
3. A textile treated by the method according to claim 1.
4. The textile according to claim 3, comprising a superfine fiber having a fineness of at most 0.8 denier.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP94/02223

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int. Cl <sup>6</sup> D06M13/292, D06M13/188, D06M15/277		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl <sup>6</sup> D06M13/292, D06M13/188, D06M15/277		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 5-98568 (Senka K.K., Daihachi Kagaku Kogyo K.K.), April 20, 1993 (20. 04. 93) (Family: none)	1, 2
Y	JP, A, 63-105175 (Kanebo, Ltd.), May 10, 1988 (10. 05. 88) (Family: none)	1
A	JP, B1, 43-13397 (Daiichi Iace K.K.), June 6, 1968 (06. 06. 68) (Family: none)	1, 2
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search April 5, 1995 (05. 04. 95)		Date of mailing of the international search report April 25, 1995 (25. 04. 95)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)